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Supporting Information

Modeling, Simulation, and Fabrication of a Fully Integrated, Acid-stable, Scalable Solar-Driven Water-Splitting System

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A. Raw Materials

The wafers were prime grade and purchased from Silicon Quest (San Jose, CA 95134). The resistivity of the n-type wafers and the p-type wafers were 10-30 ohm cm and 3-10 ohm cm, respectively. The Nafion XL was purchased from Ion Power (New Castle, DE 19720). The chassis was 3D-printed using a translucent acrylate (RGD720) by an Objet 350 Connex (Stratasys, Eden Prairie, MN 55344). The perchloric acid, Ga/In eutectic, ammonium fluoride, and butyltin trichloride were purchased from Sigma Aldrich (St. Louis, MO 63103). Inlet and outlet ports (PEEK, 0.30" ID and 0.0625" OD) were purchased from Upchurch Scientific (Oak Harbor, WA 98277). The Pharmed BPT tube was purchased from VWR (Radnor, PA 19087). The Ag-based conductive epoxy was obtained from CircuitWorks from ITW Chemtronics (Kennesaw, GA 30152).

B. Si Wafer Processing and Junction Fabrication

a. Ion Implantation

The p^+nn^+ and n^+pp^+ Si wafer devices were fabricated by ion implantation. The implantation was performed at room temperature at a 7° incident angle under high vacuum. Implantation conditions were adapted from Douglas et al,[1] and were simulated using Stopping and Range of Ions in Matter (SRIM). The implantation conditions for the emitter of the photoanode (p^+nn^+) and the photocathode (n^+pp^+) were 15 keV ^{11}B with a dose of $4x10^{14}$ cm^{-2} and 15 keV ^{31}P with a dose of $4x10^{14}$ cm^{-2}, respectively. The implantation conditions for the degenerately doped back contact layers for the photoanode and the photocathode were 15 keV ^{31}P with a dose of $5x10^{15}$ cm^{-2} and 15 keV ^{11}B with a dose of $5x10^{15}$ cm^{-2}, respectively. The SRIM simulations indicated that the junction depths would be 300 and 350 nm for the p^+n and n^+p configurations,

respectively. The dopants were activated by rapid thermal annealing at 1000 ºC for 30 s in a N_2(g)-flooded environment.

c. Silicidation

To improve the electron transport and to reduce the parasitic contact resistance between the Si and metal interface, the backside of the wafers were heavily doped to form a silicide. A titanium silicide ($TiSi_2$) and a Pt silicide ($PtSi_2$) were formed on the p^+nn^+ and n^+pp^+ wafers, respectively. In both cases, the wafers were first cleaned with BHF and then immediately sputtered with 30 nm Ti and 100 nm Pt for the n-type wafer or with 100 nm Pt for the p-type wafers. The silicide was formed during the thermal processes associated with the subsequent processing steps.

C. Faradaic O_2 Measurement on Photoanode

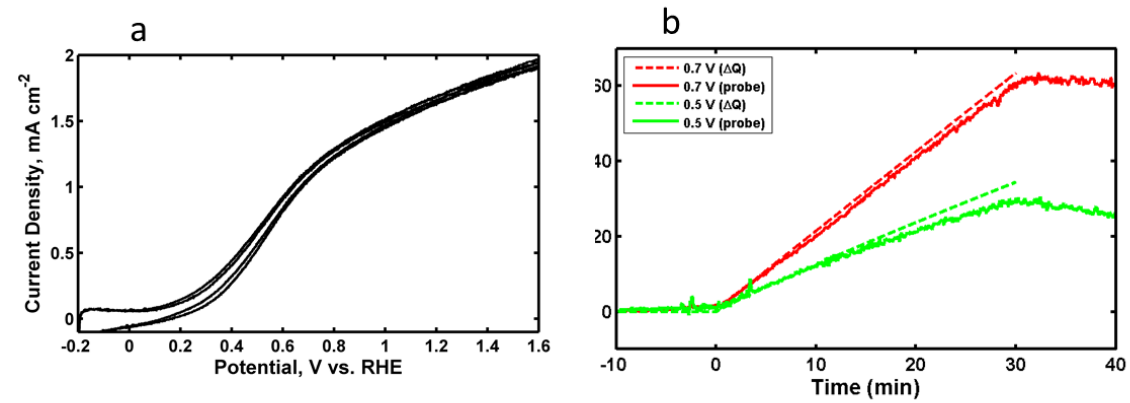

Figure S1. The photoanode in aqueous 1.0 M $HClO_4$, illuminated with simulated 100 mW cm^{-2} (a) Current density vs. voltage voltammogram and (b) oxygen generation measurement for a representative WO_3/FTO/p-n Si photoanodes.

The Faradaic oxygen measurement of the photoanode was measured as described in Spurgeon et al 2013.[2] Briefly, the dissolved oxygen concentration of the electrolyte was measured using a fluorescence-based sensor (NeoFox, Ocean Optics). The optical

probe was constructed by, inserting and sealing a fiber optic cable in one end of a glass tube and on the other end of the glass tube, close to the face of the fiber optical the O2 sensitive fluorescent patch (HIOXY, Ocean Optics) was sealed and exposed to the electrolyte. The oxygen probe was calibrated against a saturated solution of 1 M $HClO_4$ using an O_2 solubility of 7.7 mg L^{-1} under 0.21 atm of O2 partial pressure. The measurement were conducted at two working electrode potentials of 0.5 and 0.7 V vs. RHE, as shown in Figure S1. For each measurement the working electrodes were first held at open circuit potential for 10 minutes, then they were maintained at the either at 0.5 or 0.7 V vs. RHE, and again at open-circuit potential for 10 minutes. The experiments were conducted under constantly illumination at 100 mW cm^{-2} and constant stirring. Both working electrode potential show high faradaic efficiency without a co-catalyst in 1 M $HClO_4$.

[1] E. C. Douglas, R. V. Daiello *Ieee T Electron Dev*. **1980**, 27, 792-802.
[2] J. M. Spurgeon, J. M. Velazquez, M. T. McDowell *Phys Chem Chem Phys*. **2014**, 16, 3623-3631.